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Synthesis and Spectroscopic Investigation of Azoporphyrins

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Abstract: The synthesis of a series of new covalently-connected azoporphyrin derivatives is described and the photochemical properties of the new compounds are discussed. The two chromophores of these derivatives exhibit their absorption spectroscopic properties respectively. In the fluorescence emission spectra, intermolecular fluorescence quenching is detected.

Keywords: Azo-porphyrin, UV/Vis-spectra, fluorescence quenching.

Recently the synthesis of the porphyrins and the investigation of their physico-chemical properties have been of increasing interest. In particular, well-designed porphyrin derivatives can act as switches and gates[1], nonlinear optics[2] and other organic photoelectric materials[3,4]. In these fields the investigation of photoinduced electron transfer is essential in understanding the mechanism and processes of these molecular scale electronic components. Azobenzene and some azobenzene derivatives could perform *cis-trans* isomerization under photochemical reactions and might undergo energy transfer[5]. And the compounds that contain two chromophores, azo and porphyrin, have been synthesized[6-10]. But in these reports only *ortho*-azophenyl-porphyrin[6] and diporphyrins[10] showed photoinduced electron transfer. So the properties of the electronic excited state of covalently-linked two component porphyrin system needs further theoretical and experimental studies.

In this paper, we prepared the new azo-porphyrins **1** and **2**, in which the azophenyl groups were in the *para* position of the tetraphenylporphyrin and they are *di*-(**a**), *tri*-(**b**) and *tetra*-(**c**) substituted. The properties of these azo-porphyrins were investigated.

The synthesis of the new compounds is outlined in the **Scheme 1**. **3** (**a**,**b**,**c**) were prepared by the reduction of the nitro groups of 5, 10, 15, 20-tetrakis(*p*-nitrophenyl) porphyrin (TNPP) [11] with two times the stoichiometric amount of $SnCl_2$ (56% overall yield). The reaction was performed in concentrated hydrochloric acid at room temperature for 2 h and then 70°C for 30 min. After the reaction mixture was neutralized with concentrated ammonium hydroxide, the isolated solid mixture was placed in a Soxhlet apparatus and extracted with chloroform for 4-5 days to gain compounds **3**. Amino-porphyrins **3** were used without further purification to form *p*-benzenediazonium hydrochlorate solution under 0°C with $NaNO_2$ and HCl. This

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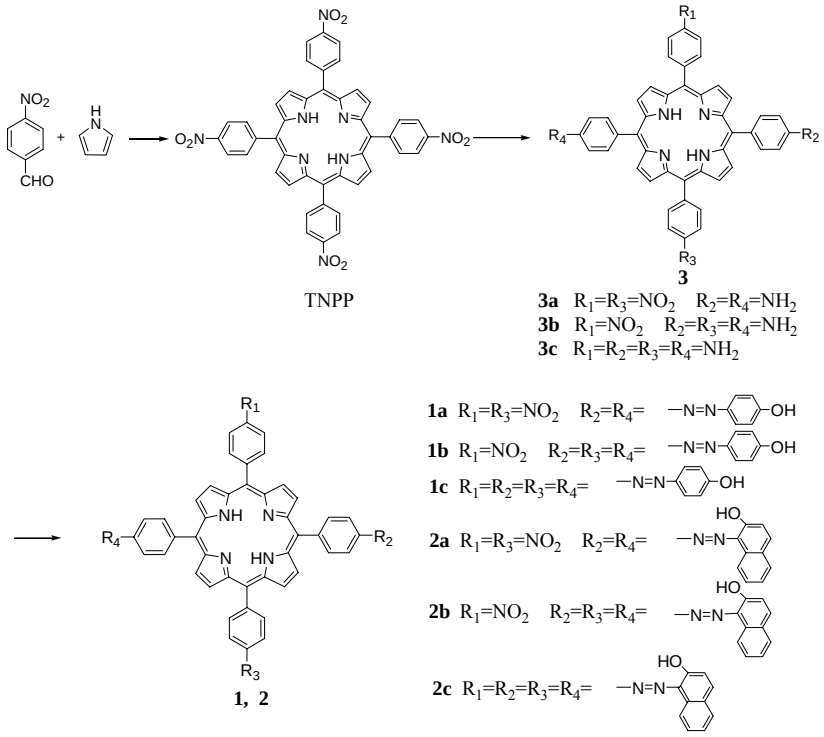
Scheme 1



solution coupled with phenol or naphthol to convert **1** or **2**. Porphyrins **1**, **2** and **3** were separated from each other by column chromatography in each about 30% yields respectively. They have been charactered by ESI-MS and ^{1}H NMR spectroscopies[12].

From the ^{1}H NMR spectra, the pyrrolic protons showed two doublets in the compounds **1a** and **2a**. This indicate that the R^1 group should be the same as R^3 while R^2 as R^4. This was similar with Vicente's result[13].

The synthesized porphyrins have interesting spectroscopic properties. From the UV-Vis absorption spectra (**Figure 1**) the porphyrin absorption bands of compounds **1** and **2** were relatively weak and broadened in the azo-aryl groups $\pi\rightarrow\pi^*$ region between

Figure 1 UV-Vis spectra of compounds **1** in ethyl acetate and **2** in chloroform (5×10^{-6}mol/L)

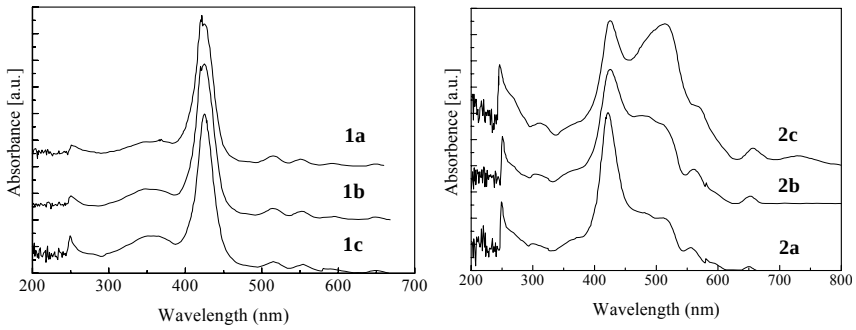


Table 1 Emission peak of porphyrins **1** and **2**

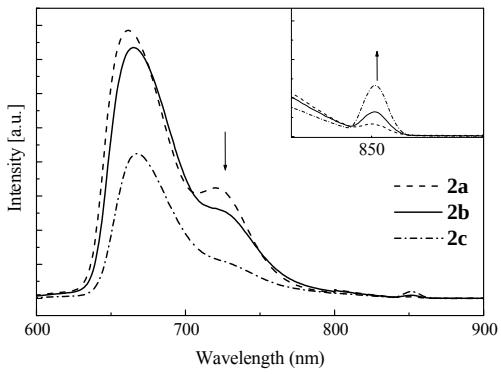
Emission peak λ(nm)	**1a**	**1b**	**1c**	**2a**	**2b**	**2c**
λ_{ex}=426 nm	654, 718	655, 718	656, 719	662, 720	665, 720	664, 723
λ_{ex}=356 nm	-	-	-	851	851.5	851.7

356 and 309 nm. In addition, according to the increase of azo-aryl group in **a**,**b** and **c** it was clear that the intensity of absorption peak at about 360 nm (309 nm) of azo-aryl group of **1** and **2** increased.

Moreover the porphyrin moiety gave a "split Soret" structure (**1a**) in which two components had about equal height. Then "split Soret" structure disappeared (**1c**) and the Soret band was slightly red shifted (6 nm) for porphyrin containing four symmetry peripheral azobenzene substituents. The Q bands of **1** showed insignificantly affected, however the azonaphthalene group peaks near 510 nm covered up the Q band of porphyrin moiety near 517 nm. The height of these peaks increased gradually, and the peaks turned to a very broad canopy-like strong band.

The fluorescence emission bands did not shift and the intensity was the same for all compounds **1**, it was in agreement with the absorption spectra with unchanged Q-bands (**Table 1**). On the other hand, this was not the case of the emission spectrum of **2**. As demonstrated in **Figure 2** the fluorescence peak intensity of **2** decreased significantly in the order of *di*-(**a**), *tri*-(**b**) and *tetra*-(**c**) azo-groups substituted compounds. The porphyrin fluorescence of **2b** and **2c** are quenched by 7% and 45%, respectively, as compared to compound **2a**. And it was clear that the emission near 720 nm reduced markedly. These results evidently indicated that substantial amount of electron transfer occured from the azonaphthalene group to the porphyrin chromophore in the excited stage. In addition, compounds **2** appeared more emission peak at 851 nm when excited at the azophenyl group absorption maximum at 356 nm. In contrast, the fluorescence peak intensity increased with the addition of the azonaphthalene substituent. From the UV-Vis and fluorescence spectrum, it was evident that porphyrins **2** might possess potential molecular sensing or photoconductive applications. More details studies of the photochemistry of these compounds are under investigation.

Figure 2 The fluorescence spectra of porphyrins **2** in chloroform (5×10^{-6}mol/L)



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12. Selected data of **3a**: ESI-MS *m/z* 735 $(M+H)^+$; ^{1}H NMR ($CDCl_3$, 300MHz, δ_{ppm}): -2.74 (s, 2H, NH), 4.04 (s, 4H, NH_2), 7.07 (d, 4H, *J*=8.1 Hz, ArH), 8.00 (d, 4H, *J*=8.1 Hz, ArH), 8.38 (d, 4H, *J*=8.4 Hz, ArH), 8.62 (d, 4H, *J*=8.4 Hz, ArH), 8.71-8.75 (m, 4H, pyrrole-H), 8.96-9.01 (m, 4H, pyrrole-H); **3b**: ESI-MS *m/z* 705 $(M+H)^+$; ^{1}H NMR ($CDCl_3$, 300MHz, δ_{ppm}): -2.73 (s, 2H, NH), 4.05 (s, 6H, NH_2), 7.06 (d, 6H, *J*=7.8 Hz, ArH), 7.97-8.01 (m, 6H, ArH), 8.38 (d, 2H, *J*=8.4 Hz, ArH), 8.61 (d, 2H, *J*=8.4 Hz, ArH), 8.69 (d, 2H, *J*=4.8 Hz, pyrrole-H), 8.93-8.97 (m, 6H, pyrrole-H); **3c**: ESI -MS *m/z* 675 $(M+H)^+$; ^{1}H NMR($CDCl_3$, 300MHz, δ_{ppm}): -2.73 (s, 2H, NH), 4.04 (s, 8H, NH_2), 7.06 (d, 8H, *J*=8.4 Hz, ArH), 7.97 (d, 8H, *J*=8.4 Hz, ArH), 8.90 (s, 8H, pyrrole-H); **1a**: ESI-MS *m/z* 943 $(M-H)^-$; ^{1}H NMR($CDCl_3$, 300MHz, δ_{ppm}): -2.76 (s, 2H, NH), 5.30 (s, 2H, OH), 7.04 (d, 4H, *J*=8.4 Hz, ArH), 8.05 (d, 4H, *J*=8.7 Hz, ArH), 8.27-8.43 (m, 12H, ArH), 8.65 (d, 4H, *J*=8.4 Hz, ArH), 8.79 (d, 4H, *J*=6.0 Hz, pyrrole-H), 8.98 (d, 4H, *J*=5.1 Hz, pyrrole-H); λ_{abs}($CH_3COOC_2H_5$) 355, 421, 426, 516, 552, 593, 649; **1b**: ESI-MS *m/z* 1018 $(M-H)^-$; ^{1}H NMR($CDCl_3$, 300MHz, δ_{ppm}): -2.72 (s, 2H, NH), 5.31 (s, 3H, OH), 7.04 (d, 6H, *J*=8.4 Hz, ArH), 8.05 (d, 6H, *J*=8.7 Hz, ArH), 8.27-8.44 (m, 14H, ArH), 8.65 (d, 2H, *J*=8.7 Hz, ArH), 8.78 (d, 2H, *J*=5.1 Hz, pyrrole-H), 8.97 (s, 6H, pyrrole-H); λ_{abs}($CH_3COOC_2H_5$) 349, 421, 426, 517, 553, 593, 649,; **1c**: ESI-MS *m/z* 1093 $(M-H)^-$; ^{1}H NMR($CDCl_3$, 300MHz, δ_{ppm}): -2.76 (s, 2H, NH), 5.32 (s, 4H, OH), 7.04 (d, 8H, *J*=8.7 Hz, ArH), 8.05 (d, 8H, *J*=8.7 Hz, ArH), 8.27-8.39 (m, 16H, ArH), 8.96 (s, 8H, pyrrole-H); λ_{abs}($CH_3COOC_2H_5$) 353, 427, 518, 554, 580, 650; **2a**: ESI-MS *m/z* 1045 $(M+H)^+$; ^{1}H NMR($CDCl_3$, 300MHz, δ_{ppm}): -2.73 (s, 2H, NH), 6.94-6.97 (m, 2H, ArH), 7.46 (m, 2H, ArH), 7.62-7.65(m, 4H, ArH), 7.79-7.82 (m, 2H, ArH), 8.15-8.18 (m, 4H, ArH), 8.33-8.44 (m, 8H, ArH), 8.62-8.70 (m, 6H, ArH), 8.80 (d, 4H, *J*=3.9 Hz, pyrrole-H), 9.01 (d, 4H, *J*=3.3 Hz, pyrrole-H), 16.60(s, 2H, OH); λ_{abs}($CHCl_3$) 303, 424, 502, 559, 580, 653; **2b**: ESI-MS *m/z* 1171 $(M+2H)^+$; ^{1}H NMR($CDCl_3$, 300MHz, δ_{ppm}): -2.69 (s, 2H, NH), 6.94-6.97 (m, 3H, ArH), 7.45-7.48 (m, 3H, ArH), 7.60-7.67 (m, 6H, ArH), 7.79-7.82 (m, 3H, ArH), 8.15-8.18 (m, 6H, ArH), 8.34-8.45 (m, 8H, ArH), 8.66-8.73 (m, 5H, ArH), 8.80-8.81 (m, 2H, pyrrole-H), 9.00 (s, 6H, pyrrole-H), 16.60 (s, 3H, OH); λ_{abs}($CHCl_3$) 305, 426, 489, 559, 580, 653; **2c**: ESI-MS *m/z* 1296 $(M+2H)^+$; ^{1}H NMR($CDCl_3$, 300MHz, δ_{ppm}): -2.69 (s, 2H, NH), 6.94-6.97 (m, 4H, ArH), 7.45-7.48 (m, 4H, ArH), 7.60-7.67 (m, 8H, ArH), 7.79-7.82 (m, 4H, ArH), 8.15-8.18 (m, 8H, ArH), 8.34-8.45 (m, 8H, ArH), 8.66-8.73 (m, 4H, ArH), 8.99 (s, 8H, pyrrole-H), 16.60 (s, 4H, OH); λ_{abs}($CHCl_3$) 309, 426, 513, 566, 656, 725.
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